



Mr. Ed Rissmann
U.S. Environmental Protection Agency
Mailstop OS-333 / Room SE-246
401 M Street, S.W.
Washington, DC 20460

January 21, 1993

Dear Ed,

Please find enclosed our responses to Great Lakes' comments on the analytical data. Most can be resolved by reference to the text pages that preceded the data tables in the original report. Our responses stick closely to the issues raised in Great Lakes' letter, which was non-CBI. We believe that this package is therefore also non-CBI.

I will be out of the office until Monday, January 25, but I will be checking my voicemail.

Sincerely,

David Smith
Chemical Engineer

TO: David Smith
Marty Huppert

FROM: Larry Pollack

DATE: January 14, 1993

RE: Response to Great Lakes Chemical Corporation - Evaluation of Record Sample Organobromine Analytical Data



SAIC has received a copy of the letter dated January 8, 1993 from Nick Macchiarolo, Plant Engineering Manager of the Great Lakes El Dorado facility, written to Edwin Rissmann of the US EPA Office of Solid Waste. Based on the comments made by Great Lakes Chemical Corporation regarding the analytical data submitted to EPA in support of the organobromine listing determination, it appears that the analytical data summary dated November 1992, and reviewed by Great Lakes, may not have included all pages prepared for the document. Five pages of the analytical data summary report included a written narrative with comments that address many of the concerns raised by Great Lakes. A copy of these pages is attached to this memo.

The following discussion has been prepared in response to the general comments listed in the January 8th letter submitted by Great Lakes to EPA.

- A. The detection of selenium appears to have been a false-positive due to the high concentrations of bromine present in most of the samples. Each sample analyzed for total or TCLP metals was analyzed using ICP-MS instrumentation. Selenium is one atomic mass unit less than bromine. High concentrations of bromine in many samples collected at Great Lakes resulted in interferences that were detected by the instrumentation and identified as selenium. In an attempt to confirm the presence of selenium, sample GL-04 was analyzed using graphite furnace atomic absorption (GFAA), SW-846 Method 7740, specific for selenium. No selenium was detected. The information from these additional analyses was discussed in the narrative included with the analytical data summary report.

All selenium results in the analytical data summary report were flagged with an asterisk (*). The flag indicates that "The result for selenium analyzed using ICP-MS instrumentation is suspected to be a false-positive." The reasoning for the occurrence of the false-positive was also discussed in the narrative provided with the data summary report.

The presence of arsenic and silver in the samples was not questioned by the laboratory. Arsenic is two atomic units less than bromine. High concentrations of bromine have not been proven to be an interferant to the determination of either arsenic or silver; however, samples with high chloride concentration in combination with argon (from the ICP argon plasma) can result in detection of arsenic. Confirmatory analyses by either flame or graphite furnace AA methods were not performed for arsenic or silver. The laboratory did not flag the arsenic or silver results as there is no indication that the arsenic values were not representative of the sample matrix. To prevent potential biasing of sample results, the laboratory does not receive details regarding the sampling location or process chemistry. Only information relating to the health and safety of laboratory personnel is transmitted (e.g., corrosive sample, percent levels of suspected carcinogens, etc).

Post-It Fax Note	7671	Date	1/23
To: Anthony Carrell	From: Mario Gendron		
Co-Dept: EPA/OSW	Co: SAIC		
Phone: 3080458	Phone: 319 4951		

- B. Equipment decontamination procedures were used prior to the collection of each sample. Final rinsings of HPLC grade water were collected and analyzed as equipment blank (EB)/QC samples. The equipment blank data demonstrate that there was no cross-contamination introduced during the sampling operations.
- C. One of the major limiting factors of all analytical instrumentation is the dynamic linear range. The concentration of the predominant constituent or constituents in a sample must be brought within the linear range of the analytical equipment prior to introduction into the instrument's detection system. Failure to calculate concentrations of detected compounds within the linear range of an instrument will result in erroneous quantitation. Diluting the sample extract prior to analysis is a widely accepted method, often used to achieve this objective.

Also, using a sample aliquot less than the method-specified sample volume is another means to prevent overload, or saturation, of instrument detection systems. If a smaller sample size was selected by the analyst to ensure accurate quantitation of the detected analytes, a "dilution factor" must be introduced to properly perform the standardized calculations. For example, if the method specifies the analysis of 10mL of sample, but only 1mL was analyzed, this would be equivalent to a dilution factor of 10. All concentrations measured by the instrument would be multiplied by 10.

- D. Laboratories selected for analysis of the samples collected in support of listing determinations were chosen based on ability to analyze samples of unusual matrices that potentially contain wide ranges of analytes and wide ranges of concentrations (part per billion, part per million, or greater, including percent levels) of organic and inorganic analytes. The laboratories possess certifications issued by national agencies which are used to evaluate the lab's ability to accurately analyze samples for correct identification of constituents and proper quantitation of sample analytes.

As an example, Triangle Laboratories, the laboratory that performed the brominated dioxin and brominated furan analyses, is one of the only commercial labs that is equipped with the necessary standard reference materials and established operating procedures for this specialized analysis.

- E. As was noted in the narrative included with the data summary report, the presence of siloxanes in some samples, including the volatile analysis of sample GL-04, is a result of some of the liquid phase bleeding off of the chromatographic column and being detected by the mass spectrometer. It does not, however, indicate that all sample analyses performed using this specific column are questionable. It is true that the sample matrix may be interacting with the GC column. The long term effect of this interaction would be retention time shifts. Internal standards are compounds that are spiked into each sample, blank, and analytical standard injected into the GC/MS system. The internal standard compounds are used to monitor retention times. Method criteria have been established that specify corrective actions should retention times exceed acceptable criteria.

Analysis of initial and continuing calibration standards prior to sample analyses also ensures that the sensitivity of the instrument has not been compromised by the sample matrices. The calibration standards include known concentrations of all target analytes and must meet criteria that demonstrate instrument stability.

Also note that the amount of hexamethylcyclotrisiloxane in sample GL-04 that bled from the column and actually was detected by the instrument was 0.167 ppm. The sample required dilution by a factor of 50,000. As discussed above under "C", all detected compounds, whether the compound is contributed to the sample through lab contamination or some other means, are multiplied by the dilution factor ($0.167 \text{ ppm} \times 50,000 \text{ dilution factor} = 8368 \text{ ppm}$ hexamethylcyclotrisiloxane).

The majority of the comments regarding specific samples consider the sources of three elements (selenium, arsenic, silver) and the sources of certain volatile constituents (e.g., methylene chloride, toluene). Also discussed were the relative concentrations of volatile organics contributed through laboratory contamination versus the actual concentration of compounds in the samples as collected at Great Lakes.

The Agency and its contractors cannot edit or remove analytical data as reported by a laboratory. The data can, however, be flagged when appropriate. In the revised version (November, 1992) of the organobromine analytical data summary report, each volatile organic analysis had a column added to the summary page. This additional information included the concentration of each compound if detected in the laboratory method blank analyzed in conjunction with the field sample. The additional data will allow the user to calculate the amount of each analyte in the sample relative to the amount present in the method blank. The calculation was performed for each analyte discussed in Mr. Macchiarolo's letter and the information is shown in Table 1.

The summary analytical data report included a written narrative that discussed target analytes detected in the laboratory method blanks. All detections of 1,1-Dichloroethene were stated to be laboratory artifacts.

Methylene chloride is a common laboratory contaminant that is used in the extraction procedure during semivolatile sample preparation. The amount of laboratory contamination relative to the amount of methylene chloride present in the field sample must be evaluated on a sample-by-sample basis.

Dibromomethane was detected in some of the method blanks, and likely resulted from sample carryover. The carryover occurred despite the laboratory's best efforts to minimize the effects of analyzing samples that contained percent levels of brominated compounds while achieving part-per-billion analysis detection limits.

Toluene was detected as a laboratory contaminant on a limited basis in some of the method blank analyses. Sample GL-04 contained enough toluene to saturate the GC/MS instrument when analyzed at 50,000-fold dilution. The sample was reanalyzed using a dilution factor of 200,000 solely to quantify toluene within the linear range of the instrument calibration. Based on the amount of toluene detected in sample GL-04, the analyte is not a laboratory artifact. Carryover of toluene to other samples (e.g., GL-02) is possible, but not supported by laboratory method blank data.

Additional information regarding sample-specific comments follows:

GL-01: The reported concentration of methylene chloride was 10 ppm and the amount of methylene chloride detected in the method blank analyzed in conjunction with the sample was 0.00334 ppm. When the amount detected in the blank is multiplied by the dilution factor (2500), it is evident that the detection of methylene chloride in GL-01 is, for all practical consideration, contributed entirely from lab contamination.

GL-03: Sample collected at 1100 hrs. on 5/18/92 and returned to the facility prior to the conclusion of the sampling event. It was determined that, due to the corrosive matrix, it could not be shipped to the laboratory. The stream was selected for sampling based on a flow diagram which indicated that it was diluted and neutralized. However, the process had been altered and the stream was now stated to be 85% acid with 1% bromine. The sample was visually characterized as being bright red and evolving brown fumes of bromine.

GL-04: The data do not imply that methylene chloride is present at a concentration of 324 ppm. The "B" flag indicates to the user that methylene chloride was detected in the method blank analyzed with the sample. To determine the relative amount of methylene chloride present in the blank for comparison to the sample concentration, the concentration in the method blank is multiplied by the dilution factor. It is true that low concentrations are magnified to appear as large values, but it is the data user's responsibility to make decisions as to whether detection of the analyte is entirely or partially due to laboratory contribution. The comparison between the method blank value multiplied by the sample dilution factor is the only practical approach to the situation.

GL-05: Benzene was detected at 0.31 ppm. The method blank analysis did include analysis for benzene but benzene was undetected. Again, taking into account the dilution factor (100), the actual amount of benzene detected by the instrument was 0.00308 ppm (0.308/100). A concentration of 3.08 ppb could be contributed from background.

The C_8H_{16} compound may be a cyclic hydrocarbon but is not an artifact from the chromatographic column. No silicon is present that is representative of siloxane compounds.

GL-06: The sample required a minimum dilution factor of 500,000 due to the concentration of the predominant volatile constituent, bromoethane. As shown in Table 1 of this memo, the concentrations of 1,1-Dichloroethene, methylene chloride, and dibromomethane are all comparable to the amount present in the method blank. The sample dilution factor is applied to all constituents including those that may have been from laboratory contribution.

Toluene was detected in one of the laboratory method blanks although that blank was not analyzed in conjunction with the analysis of GL-06. Toluene was only detected at a concentration of 0.00152 ppm in GL-06. The application of the dilution factor results in an apparent concentration of 760 ppm toluene ($0.00152 * 500,000$).

The validity of all tentatively identified compounds (TICs) was evaluated by a chemist experienced in interpretation of mass spectra. These compounds are tentatively identified against a mass spectral database containing approximately 40,000 mass spectra. The compounds are only tentatively identified since an actual standard reference material was not analyzed. Standard reference materials are analyzed only for designated target analytes. There potentially could be reactions occurring at any time from the time of sample collection to the time of sample analysis as well as

during sample analysis. However, the compounds detected in this sample do not indicate instrument or chromatographic column degradation.

GL-07: Quantitation of all tentatively identified compounds (TICs) is estimated. The TIC concentrations are based on a 1:1 relative response of the nearest eluting internal standard compound added to the sample extract prior to instrumental analysis.

GL-09: Reported concentration values for 1,2-Dibromomethane and 1,1,2-Tribromomethane are accurate. The dilution was required to quantify these two target analytes since they are the predominant volatile organic constituents confirmed present in the sample.

Tetradecyloxirane is not a siloxane compound and has no relevance to gas chromatographic liquid phase chemical composition or column breakdown. Siloxane compounds contain silicon; the oxirane compound is a three-membered ring with an oxygen atom.

Method blanks are always analyzed for all target analytes; if no method blank data were shown on the individual summary pages, this indicated that the compound was not detected in the method blank. The sample was reanalyzed for the sole purpose of quantifying 1,1,2-Tribromoethane within the established range of the standard calibration curve. This target analyte was the predominant volatile organic constituent detected in sample GL-09.

All sample analyses and data generated during the record sampling and analysis phase of the organobromine listing determination have been verified for accuracy, completeness, and method compliance. Copies of the validation summary reports have been submitted to the Agency. No significant deficiencies have been noted.

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TABLE 1

Summary of Great Lakes Samples and Laboratory Method Blank Results

Sample	Analyte	Conc. in Sample (ppm)	Dilution Factor for Sample Analysis	Relative Conc. Present in Blank (ppm)	Adjusted Conc. in Sample ²
GL-01	Methylene Chloride	10	2500	8.35	1.65
GL-02	1,1-Dichloroethene	0.00486	1	0.00426	0.00060
	Methylene Chloride	0.00213	1	0.01209	ND
GL-04	Methylene Chloride	110	50,000	81	29
	Methylene Chloride	315	200,000	324	ND
GL-05	Methylene chloride	0.128	100	0.180	ND
	Dibromomethane	0.123	100	0.187	ND
GL-05	Methylene chloride	4.16	2000	6.68	ND
GL-06	1,1-Dichloroethene	3190	500,000	2970	220
	Methylene Chloride	1207	500,000	810	397
	Dibromomethane	1192	500,000	3515	ND
GL-07	Methylene chloride	0.00130	1	0.00153	ND
	Dibromomethane	0.00387	1	0.00173	0.00214

¹ Method blank concentration multiplied by sample dilution factor.

² Adjusted concentration of analyte in method blank subtracted from concentration in sample.

ND = Not Detected; the amount detected in the method blank exceeds the amount detected in the field sample.

Sample	Analyte	Conc. in Sample (ppm)	Dilution Factor for Sample Analysis	Relative Conc. Present in Blank (ppm)	Adjusted Conc. in Sample?
GL-07	Toluene	0.01352	1	0.00265	0.01087
	1,1-Dichloroethene	0.0636	10	0.0849	ND
	Methylene chloride	0.0376	10	0.0153	0.0223
GL-08	1,1-Dichloroethene	0.0625	10	0.0849	ND
	Methylene chloride	0.0337	10	0.0153	0.0184
	Dibromomethane	0.0562	10	0.0173	0.0389
GL-09	1,1-Dichloroethene	174	25,000	212	ND
	Methylene chloride	27.1	25,000	38.2	ND
	Dibromomethane	73.7	25,000	43.2	ND
GL-09 (RE)	Toluene	28.5	25,000	66.2	ND
	1,1-Dichloroethene	147	25,000	148	ND
	Methylene chloride	51.0	25,000	40.5	10.5
	Dibromomethane	52.0	25,000	176	ND

1 Method blank concentration multiplied by sample dilution factor.

2 Adjusted concentration of analyte in method blank subtracted from concentration in sample.

ND = Not Detected; the amount detected in the method blank exceeds the amount detected in the field sample.

Example calculation used for comparing concentration of target analyte in method blank to concentration of target analyte detected in sample:

Sample GL-01 - Methylene Chloride

Concentration in sample = 10 ppm

Dilution factor for sample analysis = 2500

Concentration of analyte detected in method blank = 0.00334 ppm

Relative concentration present in blank = 8.35 ppm

$$(2500 * 0.00334) = 8.35$$

Adjusted concentration in sample = 1.65 ppm

$$(10 - 8.35) = 1.65 \text{ ppm}$$

Attachment 1

GREAT LAKES CHEMICAL CORPORATION

Organobromine Record Sampling & Analysis

Narrative - Analytical Data Summary Report (November, 1992)



Notes on Data Summary Forms for Record Sample Analytical Results

General

All concentrations of detected constituents are reported on an "as received, wet weight" basis which does not account for any moisture content in the solid or semi-solid samples. Percent moisture determinations would not be applicable to these samples matrices since high concentrations of volatile organics would also be released in addition to any water vapor during the drying procedure at 105°C. This would result in an erroneously high percent moisture value.

Tentatively Identified Compounds [TIC] for volatile and semivolatile compounds are only estimated values as each nontarget compound is quantified from the response of the closest internal standard compound. The identifications are only tentative based on 1) the Probable Best Match search routine performed by the instrument data system software using the EPA/NIST mass spectral database library, and 2) GC/MS analyst mass spectral data interpretation of the computer output.

Volatile Organic Analysis

1) When a sample requires dilution prior to analysis to prevent the instrument from being saturated due to excessive concentrations of organic compounds, a "D" flag is assigned to the target analytes confirmed present. The compound is reported on the data summary with a "D" following the concentration to signify that the quantitation was performed from analysis of a diluted sample. (e.g., 120 D, which indicates 120 ug/L of a target compound quantified from a sample diluted prior to analysis).

If a sample is injected and analytes are detected that exceed the range of the standard calibration curve, the concentration of the analyte is flagged with an "E" on the data summary. The concentration of the analyte calculated is not accurate and the sample must be reanalyzed. Reanalysis is performed at an appropriate dilution to ensure quantitation of the compound within the linear range of the instrument. The reanalyses of samples requiring further dilution after the initial analysis have been reported on the header of the data summary form with "/DIL".

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Volatile Organic Analysis (Continued)

2) Detection of siloxanes (e.g., hexamethylcyclotrisiloxane) as tentatively identified compounds in the volatile fraction is likely an artifact of the gas chromatographic separation. Siloxanes constitute part of the liquid phase that coats the internal diameter of a gas chromatography column used to separate the mixture of organic compounds. Certain samples can strip the siloxanes from the column, especially if the matrix is very acidic or alkaline. The compounds would not be detected under normal circumstances during analyses of laboratory QC blanks.

3) The volatile target analyte, 1,1-dichloroethene, was detected in the field samples and appears to be a laboratory contaminant. A comparable concentration of 1,1-dichloroethene was detected in the laboratory QC blanks analyzed in conjunction with the field samples.

Semivolatile Organic Analysis

The tentative identification of "Unknown Dioic Acid" is listed throughout the semivolatile data. This compound was misidentified and is actually the surrogate compound, tetrafluorophenol. Tetrafluorophenol was used in place of 2,4,6-tribromophenol. Surrogate compounds should not be library searched and reported as a tentatively identified compound. Pacific Analytical will be requested to submit revised data summary forms.

Inorganic Analyses

All eight inorganic target analytes were listed on each of the metals data summary pages provided in Section I of this Appendix. The results list the concentration of the analyte if confirmed present, in addition to the detection limits of elements not confirmed present.

Selenium was reported as a false positive in the inorganic analyses performed using ICP-MS instrumentation. The results have been flagged with an asterisk (*) on the data summary forms provided in Section I of this Appendix. The flag indicates that the result is suspect. To confirm that selenium was not present in the field samples, two samples that contained large concentrations of brominated compounds were selected for further confirmatory analyses. Samples ET-02 and GL-04 were analyzed for selenium using Graphite Furnace Atomic Absorption (GFAA) techniques. No selenium was confirmed present by GFAA indicating that the detection of selenium using ICP-MS resulted from the similar atomic weight of these two elements (bromine is one mass unit greater than selenium).

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Flags

- D - concentration of analyte quantified from analysis of a diluted sample.
- E - concentration of analyte exceeds the established linear range of the standard calibration curve.
- B - compound detected in the laboratory QC blank extracted/analyzed in conjunction with the field sample.
- U - compound was not detected; concentration listed in the method calculated detection limit.
- J - compound was detected and confirmed present; concentration is less than the method calculated detection limit.
- * - result for selenium analyzed using ICP-MS instrumentation is suspected to be a false-positive.

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Notes on Record Samples

TB-01: Trip blank collected 10:00 5/18/92. Taken at facility entrance, outside process area.

GL-01: Collected 10:15 5/18/92. Label says 09:45, but the sampling team then remembered that a trip blank needed to be taken first. Aqueous phase from the bottom of the methanol/water separation column in the tetrabromobisphenol A unit. Stream emerges at 210 °F. No HDPE bottles used for metals portion because the heat would damage them. Amber bottles used instead. As sample cooled, masses of white crystals formed, believed to be tribromophenol or bisphenol A.

GL-02: 11:00 5/18/92. Filtrate from the belt filter in the decabromodiphenyl oxide unit. Facility personnel indicated that this has a pH of about 4. Should contain diphenyl oxide, phenols, and brominated derivatives of them.

GL-03: 11:00 5/18/92. Spent sulfuric acid from the bromine dryer in the decabromodiphenyl oxide unit. Produced from 98% acid by using it to dry bromine vapor over a period of about 5 hours. An 85% acid stream with 1% bromine. Bright red, extremely corrosive, and evolving brown fumes of bromine. This sample was returned to the facility after it was determined that it could not be shipped or analyzed. Stream was selected for sampling based on a flow diagram which indicated that it was diluted and neutralized. Process was recently altered.

GL-04: 12:15 5/18/92. Filter cake from filtration of toluene/product solution in the octabromodiphenyl oxide plant. A granular, speckled black solid collected in bag filters. One bag filter was selected from a dumpster and the contents spooned out.

GL-05: 12:45 5/18/92. Wastewater from the toluene/product decant in the octabromodiphenyl oxide unit. A cloudy, yellowish water.

GL-06: 13:40 5/18/92. Spent activated alumina from purification of ethyl bromide. The alumina is used principally to adsorb water. Light grey pellets, about 1/8 inch diameter.

EQ-01: 14:15 5/18/92. Equipment blank generated after rinsing sampling spoon.

FB-01: 15:00 5/18/92. Field blank.

TB-02: 10:55 5/19/92. Trip blank.

GL-07: 11:15 5/19/92. Sump solids from the tetrabromophthalic anhydride unit. Solids are packed in 55-gal drums with a layer of dry cement powder on top to absorb water. Sample has the consistency and color of toothpaste, but is very dense. May be acidic. Contains high concentrations of tetrabromophthalic anhydride, may require special preparative work. Sample could not be put into VOA vials.

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GL-08: 12:45 5/19/92. Activated carbon used to purify hydrogen bromide in the tribromophenol unit. A fine granular black solid with a few white specks.

GL-09: 11:45 5/19/92. Floor sweepings from the tribromophenol unit. A mixture of coarse powders of various colors, of which the tribromophenol was the white component.

[No field blank collected on 5/19/92 because no liquids were collected.]

TB-03: 09:30 5/20/92. Trip blank.